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㉕ Applicant: SHELL INTERNATIONALE  
RESEARCH MAATSCHAPPIJ B.V.  
Carel van Bylandtlaan 30  
NL-2596 HR Den Haag(NL)

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㉗ Inventor: Drent, Eit  
Badhuisweg 3  
NL-1031 CM Amsterdam(NL)

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㉙ Process for the telomerization of conjugated alkadienes.

㉚ A process for the telomerization of conjugated alkadienes which comprises contacting a conjugated alkadiene with a compound having at least one active hydrogen atom, in the presence of a catalyst obtainable from a palladium compound and a diphosphine of general formula  $R^1R^2PRPR^3R^4$ , wherein R is a bivalent organic bridging group containing at least 3 atoms in the bridge, of which at least two are carbon atoms;  $R^1, R^2, R^3$  and  $R^4$  are the same or different and represent optionally polar substituted hydrocarbyl groups.

EP 0 542 366 A1

The present process relates to a process for the telomerization of conjugated dienes, and more in particular to such a process conducted in the presence of a catalyst based on a palladium compound and a phosphine ligand, and to the products thus prepared.

Telomerization is a known reaction and refers to the reaction of conjugated alkadienes in the presence of a compound having an active hydrogen, such as for example a hydroxy compound, a primary or secondary amine, a carboxylic acid, a compound containing an active methylene group, and water.

The telomerization of conjugated alkadienes is known for example from Dutch Patent Specification 156 387, which document relates to the oligomerization of specified conjugated dienes in the presence of a compound containing active hydrogen and a catalyst based on a combination of a bivalent palladium compound and a phosphine or arsine. Although both mono- and diphosphines and arsines are claimed, there appears to be a strong preference for the use of monophosphines, and especially triphenyl-phosphines. In fact in all the examples the catalyst either is based on a monophosphine or a monoarsine. From the large number of examples provided it can be observed that an acceptable degree of alkadieneconversion and/or the selectivity to the desired reaction product is only obtained when the active hydrogen containing compound employed is an organic hydroxy compound. When using other types of active hydrogen containing compounds the alkadiene conversion and selectivity leave considerable room for improvement.

As mentioned hereinbefore water is also considered to be an active hydrogen containing compound for use in telomerization reactions, as it offers the possibility of converting the alkadienes to the corresponding hydroxy dimercompounds, which compounds may be used e.g. in organic synthesis. The only information provided in said Dutch Patent Specification regarding the use of water is as a solvent.

The preparation of 2.7-octadienol-1 via a catalytic telomerization of butadiene in the presence of water is known from Russian Patent Application SU 979-316-A. Said method however, has a disadvantage in that it employs a rather complicated multicomponent catalyst system which comprises a specified metal sulphate, a palladium salt, a phosphine (such as an alkyl or aryl monophosphine) or a phosphine and an organo-aluminium reducing agent.

It will be appreciated that the known catalyst system based on a palladium compound and a monophosphine such as for example triphenylphosphine, will be less stable and thus have a shorter life time, than similar catalyst systems containing chelating ligands such as for example 1.2-bis-(diphenylphosphino)ethane.

Hence it can be concluded that there is considerable need for improvement in the telomerization of alkadienes. The problem underlying the present invention is to develop a process for the telomerization of alkadienes which does not suffer from one or more of the disadvantages as described hereinbefore. Thus, there is a need to develop a process for the telomerization of alkadienes which is conducted in the presence of active hydrogen-containing compounds, which combines a high alkadiene conversion with a high selectivity and/or which can be conducted in the presence of a relatively simple catalyst system.

As a result of extensive research and experimentation it was now found that the telomerization of alkadienes in the presence of an active hydrogen-containing compound could conveniently be conducted in the presence of a catalyst based on a palladium compound and selected diphosphines.

Accordingly the invention provides a process for the telomerization of conjugated alkadienes which comprises contacting a conjugated alkadiene with a compound having at least one active hydrogen atom, in the presence of a catalyst obtainable from a palladium compound and a diphosphine of general formula  $R^1R^2PRPR^3R^4$ , wherein R is a bivalent organic bridging group containing at least 3 atoms in the bridge, of which at least two are carbon atoms;  $R^1, R^2, R^3$  and  $R^4$  are the same or different and represent optionally polar-substituted hydrocarbyl groups.

Preferably the bridging group R of the diphosphine mentioned hereinbefore contains 3 to 5 atoms in the bridge. Examples of suitable bridging groups R include  $-(CH_2)_3-$ ,  $-(CH_2)_4-$ ,  $-CH_2-C(CH_3)_2-CH_2$  and  $-CH_2-Si(CH_3)_2-CH_2-$ .

The hydrocarbyl groups  $R^1, R^2, R^3$  and  $R^4$  are preferably the same and represent an aryl group, a phenyl group being the preferred aryl group, or an alkyl group having up to 10 carbon atoms. Preferred alkyl groups have from 2 to 5 carbon atoms and may be linear or branched as exemplified by ethyl, propyl, isopropyl, butyl, tert-butyl and pentyl. Preferred diphosphines for use in the process of the present invention are 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, 1,3-bis-(diethylphosphino)propane, 1,3-bis(diisopropylphosphino)propane, 1,3-bis(di-n-butylphosphino)propane and 1,4-bis(di-n-butylphosphino)butane.

The palladium compound on which the catalyst in the process of the present invention is based is preferably a palladium salt of a carboxylic acid, and palladium acetate in particular.

The conjugated alkadienes which may be converted by the process of the present invention will generally have from 4 to 8 carbon atoms and include 1,3-butadiene, isoprene, 1,3-pentadiene, 2,4-hexadiene and 2,3-dimethylbutadiene-1,3; 1,3-butadiene is a preferred conjugated alkadiene.

A wide range of compounds having an active hydrogen such as for example alcohols, hydroxy-  
5 aromatic compounds, primary and secondary amines, carboxylic acids, compounds having an active methylene group and water, may conveniently be used in the process of the present invention. The nature of the main reaction product which may be prepared by the process of the present invention will generally comprise an adduct of the active hydrogen-containing compound and a triene which compound can be considered to have been obtained by dimerization of the relevant conjugated diene. Hence the reaction  
10 product will for example be an alcohol when water has been used as the active hydrogen containing compound, an ether when an alcohol is used, a secondary or tertiary amine when respectively a primary or secondary amine is used. In general, the hereinbefore described reaction products will be present as admixtures with minor amounts of the corresponding triene. In the present process water and primary or secondary amines are the preferred active hydrogen-containing compounds.

15 In the process of the present invention the diphosphines are preferably used in a quantity of from 0.2 to 10 and in particular from 0.5 to 5 mol per gram atom of palladium. The palladium compound will generally be employed in an amount which corresponds with a ratio in the range of from  $10^{-6}$  to  $10^{-1}$  and preferably from  $10^{-5}$  to  $10^{-2}$  gram atom of palladium per mol of conjugated alkadiene.

20 The process may conveniently be conducted in the presence of one or more inert solvents and/or diluents. Suitable solvents and/or diluents include ketones, such as acetone; ethers, such as dioxane, tetrahydrofuran, anisole (methyl phenyl ether) and diglyme (dimethyl ether of diethylene glycol); hydrocarbon compounds, such as benzene, toluene, cyclohexane and n-hexane; and polar compounds such as dimethylformamide and dimethylsulfoxide. Occasionally water may also be used as a solvent or diluent.

25 When employing water as the active hydrogen-containing compound in the process of the present invention there is a strong preference to conduct the telomerization reaction in the presence of carbon dioxide; very good results having been obtained when  $CO_2$  is present in an amount which corresponds with a  $CO_2$  pressure in the range of 500 to 5000 kPa.

When in the process of the present invention a primary or secondary amine is used as the active hydrogen-containing compound, it is preferred that the diphosphine is a bis(dialkylphosphino) based diphosphine and especially a bis(di-n-butylphosphino) or bis(diisopropylphosphino) based diphosphine. On the other hand when water is employed as the active hydrogen-containing compound, both bis-(diarylphosphino) and bis(dialkylphosphino) based diphosphines have resulted in a high conjugated diene conversion and a high selectivity to the linear alcohol type reaction product.

30 The process of the present invention will generally be conducted at a temperature in the range of from 20 to 180 °C and preferably in a range of from 50 to 150 °C.

The pressure at which the present invention is conducted will generally be in the range of from atmospheric pressure to 10000 kPa, taking in account of course the hereinbefore mentioned preferred presence of carbon dioxide when employing water as the active hydrogen-containing compound.

35 The telomerization products prepared can be recovered for example via fractionation, distillation and/or crystallization, and may advantageously be employed as such or used for example for the synthesis of polymers, synthetic resins, epoxy compounds and surface-active agents.

40 When water is the active hydrogen-containing compound, the telomerization product (dienol) can be hydrogenated to the corresponding alcohol and subsequently dehydrated to the corresponding alkene. For example, product 3,7-diene-octanol can be hydrogenated to octanol and subsequently dehydrated to 1-octene.

45 The invention will be further illustrated with the following examples which should however not be considered as limiting the scope of the invention or the manner wherein it may be practised.

The following information is provided for the examples and comparative experiments:

Di- and monophosphines used in Tables I and II

Code	Phosphine type
a)	1,3-bis(di-n-butylphosphino)propane
b)	1,3-bis(diphenylphosphino)propane
c)	1,2-bis(diphenylphosphino)ethane
d)	1,3-bis(diisopropylphosphino)propane
e)	1,4-bis(diphenylphosphino)butane
f)	1,4-bis(di-n-butylphosphino)butane
g)	triphenylphosphine

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Amines used

20	p)	n-butylamine
	q)	diethylamine

25 Example I

30 Into a 250 ml stainless steel (Hastelloy C) autoclave equipped with a magnetic stirrer were introduced 0.25 mmol Pd(OAc)<sub>2</sub>, 0.37 mmol 1,3-bis(di-n-butylphosphino)propane (a), 40 ml anisole and 10 ml n-butylamine. Subsequently the reactor was closed and the air evacuated therefrom, whereupon 10 ml 1,3-butadiene were introduced, and the reactor contents heated to 125 °C, which temperature was maintained for 5 hours. Subsequently the reactor contents were cooled to 20 °C. Analysis by gas liquid chromatography (g.l.c.) indicated that 56% of the butadiene had been converted to a mixture of N-(octadienyl-2,7)-n-butylamine(53%), N,N-di-(octadienyl-2,7)-n-butylamine(29%) and n-octatriene-1,3,7(24%).

35 Examples II - V

40 The procedure of Example I was repeated with the exception of a change in diphosphine and/or a replacement of the 10 ml of n-butylamine with 15 ml of diethylamine and/or a change in the reaction temperature, as has been indicated in Table I, which Table also presents the product data obtained.

Comparative experiments A and B

45 The procedure of Example I was repeated with the exception that 1,3-bis(diphenylphosphino)ethane (c) was used as ligand, while in experiment A the reaction temperature was 135 °C and in experiment B 15 ml of diethylamine were employed. The process details and product data have been included in Table I.

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Table I

Example	Phosphine type	Amine type	Temp °C	Butadiene conversion			Product composition		
				sec. amine	tert. amine	triene	sec. amine	tert. amine	triene
I	a	p	125	56	53	29	29	24	24
II	b	p	125	25	50	12	12	30	30
III	b	q	135	25	-	90	90	8	8
IV	a	q	100	78	-	95	95	5	5
V	d	q	100	93	-	92	92	7	7
Comp. exp.									
A	c	p	135	20	50	20	20	25	25
B	c	q	125	< 5	-	traces (~1:1)			

## Examples VI - X

To an autoclave of the type as described in Example I was added, 0.25 mmol Pd(OAc)<sub>2</sub>, 0.37 mmol of a diphosphine as indicated in Table II hereinafter, 5 ml water and 40 ml diglyme.

After closing the reactor and evacuating the air therefrom, 10 ml of 1,3-butadiene were added which was followed by pressurizing the reactor with carbondioxide to a pressure corresponding with the value indicated in Table II. The reactor contents were heated to 110 °C and maintained at this temperature for 5 hours. Subsequently the reaction contents were cooled to 20 °C and analyzed via g.l.c. Reaction details and product data have been collected in Table II.

## Comparative experiments C - E

The procedure of Examples V - X was repeated with the exception that 1,2-bis(diphenylphosphino)-ethane (c) (0,37 mmol) or triphenylphosphine (g) (0,7 mmol) was used as the phosphine compound.

Process details and the corresponding product data have been included in Table II.

From the results obtained in Examples I to V (Table I) and those obtained with the comparative experiments A and B, it can be observed that the use of diphosphines having at least 3 atoms in the bridge as described hereinbefore, and especially the bis(dialkylphosphino) based diphosphines can result in very high conjugated diene conversions in combination with a high selectivity to the telomerized products.

5 A similar phenomenon can be observed when comparing the results of Examples VI - X (Table II) with those of comparative experiments C and E.

Finally it can be concluded that as the catalyst systems of the process of the present invention are based on chelating ligands, they will be more stable than the corresponding systems based on mon-  
10 ophosphines.

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Table II

Example	Phosphine type	CO <sub>2</sub> pressure	Temp °C	Butadiene conversion %	Product composition		
					primary alcohol %	secondary alcohol %	triene %
VI	a	1000	110	88	70	7	22
VII	a	2000	110	92*	80	6	12
VIII	b	1000	110	85	71	7	20
IX	e	1000	110	92	67	6	25
X	f	1000	110	90	61	6	30
Comp. exp.							
C	c	2000	110	5	~50	~5	~45
D	g	2000	110	95	55	12	30
E	g	1000	110	85	49	9	40

\* The reaction medium included 10 ml triethyl amine

## Claims

55 1. A process for the telomerization of conjugated alkadienes which comprises contacting a conjugated alkadiene with a compound having at least one active hydrogen atom, in the presence of a catalyst obtainable from a palladium compound and a diphosphine of general formula R<sup>1</sup>R<sup>2</sup>PRPR<sup>3</sup>R<sup>4</sup>, wherein R is a bivalent organic bridging group containing at least 3 atoms in the bridge, of which at least two are carbon atoms; R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup> and R<sup>4</sup> are the same or different and represent optionally polar substituted

hydrocarbyl groups.

2. A process as claimed in claim 1, wherein the bridging group R is an alkylene group containing from 3 to 5 carbon atoms in the bridge.

5 3. A process as claimed in claim 1 or 2, wherein R<sup>1</sup>,R<sup>2</sup>,R<sup>3</sup> and R<sup>4</sup> are the same and represent an aryl group or an alkyl group having up to 10 carbon atoms and preferably from 2 to 5 carbon atoms.

10 4. A process as claimed in any one of claims 1 to 3, wherein the diphosphine is selected from the group consisting of 1,3-bis(diphenylphosphino)propane, 1,4-bis(diphenylphosphino)butane, 1,3-bis-(diisopropylphosphino)propane, 1,3-bis(di-n-butylphosphino)-propane and 1,4-bis(di-n-butyl-phosphino)butane.

15 5. A process as claimed in any one of claims 1 to 4, wherein the palladium compound is a palladium carboxylate and preferably palladium acetate.

6. A process as claimed in any one of claims 1 to 5, wherein the diphosphine is present in a ratio of from 0.2 to 10 and preferably in a ratio from 0.5 to 5 mol per gram atom of palladium.

20 7. A process as claimed in any one of claims 1 to 6, wherein the palladium compound is employed in a ratio in the range of from 10<sup>-6</sup> to 10<sup>-1</sup> and preferably from 10<sup>-5</sup> to 10<sup>-2</sup> gram atom of palladium per mol of conjugated alkadiene.

8. A process as claimed in any one of claims 1 to 7, wherein the alkadiene is 1,3-butadiene.

25 9. A process as claimed in any one of claims 1-8, wherein the active hydrogen containing compound is water, and which is conducted in the presence of carbon dioxide.

30 10. A process as claimed in any one of claims 1-9, wherein the active hydrogen containing compound is a primary or secondary amine and the diphosphine is a bis(dialkylphosphino) based diphosphine and preferably a bis(di-n-butylphosphino) or a bis(diisopropylphosphino) based diphosphine.

35 11. A process as claimed in any one of claims 1 to 10, which is conducted at a temperature in the range of from 20 to 180 °C and preferably in a range of from 50 to 150 °C, and at a pressure in the range of from atmospheric pressure to 10000 kPa.

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EUROPEAN SEARCH REPORT

Application Number

EP 92 20 3452

DOCUMENTS CONSIDERED TO BE RELEVANT			
Category	Citation of document with indication, where appropriate, of relevant passages	Relevant to claim	CLASSIFICATION OF THE APPLICATION (Int. Cl.5)
Y	GB-A-1 256 357 (MITSUBISHI CHEMICAL INDUSTRIES) * claims 11-31 * & NL-C-156 387 ---	1-8, 11	C07C29/36 C07C209/60 C07B41/02 C07B43/04 C07B61/00
D, Y		1-8, 11	
X	BULLETIN OF THE CHEMICAL SOCIETY OF JAPAN vol. 45, no. 4, April 1972, TOKYO JP pages 1183 - 1191 K. TAKAHASHI ET AL 'PALLADIUM-CATALYZED REACTIONS OF 1,3-DIENES WITH ACTIVE METHYLENE COMPOUNDS. IV. PALLADIUM-DIPHOSPHINE COMPLEX CATALYSTS' * table 3 * * page 1184 *	1-4, 6, 8, 11	
Y	---	1-8, 11	
P, X	TETRAHEDRON LETTERS. vol. 33, no. 14, 31 March 1992, OXFORD GB pages 1831 - 1834 B. M. TROST ET AL 'ATOM ECONOMY. A SIMPLE Pd CATALYZED ADDITION OF PRONUCLEOPHILES WITH DIENES' * the whole document *	1-4, 11	
A	US-A-3 530 187 (T. M. SHRYNE) * column 3, line 46 - column 4, line 39; claims; examples *	1-11	C07C C07B
A	US-A-4 120 901 (C. F. HOBBS ET AL) * table II *	1-11	
A	EP-A-0 361 304 (MITSUBISHI KASEI) * page 3, line 29 - line 34; claims; examples *	1-9, 11	
A	GB-A-2 074 156 (KURARAY) * claims 1,7; examples 20,21 *	1-9, 11	
The present search report has been drawn up for all claims			
Place of search	Date of completion of the search	Examiner	
THE HAGUE	26 FEBRUARY 1993	WRIGHT M.W.	
CATEGORY OF CITED DOCUMENTS		T : theory or principle underlying the invention E : earlier patent document, but published on, or after the filing date D : document cited in the application L : document cited for other reasons ..... & : member of the same patent family, corresponding document	
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